



# SYNTHESIS AND CHARACTERIZATION OF SODIUM ALUMINIUM SILICATE HYDRATE NANOCRYSTALS

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## ABSTRACT

Sodium aluminium silicate hydrate nanocrystals have been successfully prepared through Co-precipitation method. The effect of temperature, time, precursor and a key role of aluminium source on the sodium aluminium silicate hydrate nanocrystals properties was explored in this work. The  $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  nanocrystals obtained were systematically characterized by X-Ray Diffraction (XRD), Energy Dispersive X-ray Analysis (EDAX), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform InfraRed spectroscopy (FT-IR), UV-visible spectroscopy and Photoluminescence spectroscopy (PL). The XRD result revealed that the prepared sample possess a Nanocrystals structure which was cubic in structure and it was found that the average crystallite size was  $\sim 17$  nm. UV-Vis analysis also confirms that the prepared particles was also nano in size. The morphology of the prepared sample was investigated by SEM which showed that the particles prepared was spherical in shape and was confirmed by HR-TEM. Further, the prepared samples were characterized by PL for its luminescence property and TG-DSC for its thermal stability.

**KEYWORDS:** Sodium Aluminium Silicate Hydrate Nanocrystals, Co-Precipitation Method, Entity Characterization

## 1. INTRODUCTION

Nanotechnology is a multidisciplinary field that involves the integration of various disciplines such as technology and science[1]. In recent times Nanocrystals that is, the mean size of a crystals  $\sim 1$  to  $10$  nm which paves a great interest, in electrical and optical properties, and also materials with Nanocrystalline properties act as optically homogeneous solids[2]. The turning point in material research was the development of Nanocrystals with novel and improved properties[3].

5000 years ago natural zeolites are formed due to the chemical reaction of saline water and volcanic glass, but to produce zeolite in a short time the synthesis of zeolites were developed manually with low natural contamination and in high purity[4]. Zeolites, made up of crystalline aluminium silicate is one of the most important highly porous minerals were commonly used in petrochemical industries as catalyst and used for removing the inorganic toxins in water treatment field[5][4]. Various methods have been reported in literature for the synthesis of sodium aluminium silicate (zeolites) Nanocrystalline materials viz., Hydrothermal treatment[4],[6], Microwave and Fusion method[7].

In the current study the sodium aluminium silicate Nanocrystals was synthesized via the Co-precipitation method. The main aim was to fabricate the sodium aluminium silicate hydrate Nanocrystals material and to investigate details about the phase analysis, particle size, microstructural studies, surface composition, morphological characterization, physical and optical property of sodium aluminium silicate Nanocrystals using XRD, UV, EDAX, FTIR, SEM, TEM, PL and TG-DSC.

## 2. EXPERIMENTAL

### 2.1. Chemicals

Sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) (99.9%, VITSEEE), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) (99.9%, SYSTEM), polyvinylpyrrolidone ( $\text{C}_6\text{H}_9\text{NO}$ )<sub>n</sub> (LOBA), acetic acid ( $\text{CH}_3\text{COOH}$ ) (SPECTRUM) was used, as purchased without any further purification.

### 2.2. Synthesis

The sodium aluminium silicate hydroxide Nanocrystals were synthesized using inorganic method. The  $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  Nanocrystals was prepared by Co-Precipitation method. The method of preparation was as shown in Figure (1).

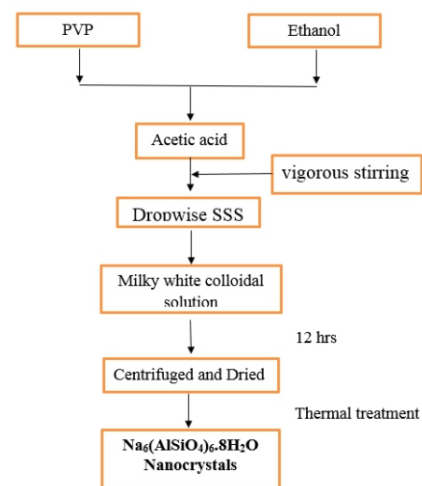


Figure 1: Flow chart for the preparation of  $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  Nanocrystals

### Preparation of sodium aluminium silicate hydrate nanocrystals:

6ml of sodium silicate solution was dissolved in 20ml of distilled water to get the diluted Sodium Silicate Solution (SSS) which was used as a precursor. The Polyvinylpyrrolidone (PVP) (3g) was used as a starting chemical which was dissolved in 15ml of ethanol. This mixture was stirred for about 10 minutes which results in clear solution which was shown in Figure (2a). A 5ml of acetic acid, used as a catalyst was added to the previous clear solution and was given a vigorous stirring for about 30 minutes at  $80^\circ\text{C}$  with an rpm of 400-500 range. Then the SSS solution was added dropwise to the prepared stock solution. The solution was stirred continuously for about 1 hour with the same rpm range. The clear solution now slowly turned to milky white colloidal solution which was shown in Figure (2b) and was allowed to rest for 12 hours without any disturbance Figure (2c).



Figure 2: Stirring process (a) PVP+Ethanol+Acetic acid (b) after adding SSS to PVP+Ethanol+Acetic acid (c) resultant colloidal solution

The supernatant liquid was removed and white precipitate was washed with distilled water for several times to remove the water soluble impurities[8]. Again, the washed precipitate was centrifuged at 1000rpm for 1hour. Then the sediments were transferred to a petri dish and dried in oven at 100 °C until the particles loose its complete moisture. Then the obtained nanoparticles were transferred to a silica crucible which was subjected to a thermal treatment in oven at 100 °C for 5 hrs. The whole process was proceeded at ambient temperature and was covered using aluminium foil. There was a change in color of the sample before and after thermal treatment which was shown in Figure (3). It was evident from the Figure (3), that the before heat treatment the product was white in color and after the heat treatment it changed into beige orange color.

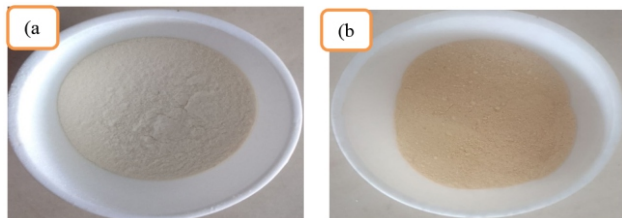


Figure 3. Resultant product (a) before heat treatment (b) after heat treatment

### 2.3 Characterization

The structural properties of prepared sample were studied using X-Ray Diffraction (XRD) analysis. XRD patterns were recorded by Bruker D8 Advance. SEM- EDAX was obtained using Jeol 6390LA/ OXFORD XMX N with Accelerating voltage 0.5 to 30 kV using Tungsten as filament. The measurement of UV-Visible absorption spectra and FTIR was performed by Perkin Elmer Lambda 365 in the range of 200 nm to 1000 nm and Thermo Nicolet iS50 4000  $\text{cm}^{-1}$  to 100  $\text{cm}^{-1}$  with resolution 0.2 $\text{cm}^{-1}$  respectively. The size and shape of a nanocrystals was measured using HRTEM Jeol/JEM 2100 at 200kV with Point and lattice resolution 0.23 nm and 0.14 nm respectively. These studies were carried out from The Sophisticated Analytical Instruments Facility (SAIF), Cochin, Kerala, India. The thermal analysis was performed using STA449 F3 Jupiter from Netzsch and Photoluminescence study was performed using JASCO Spectrofluorometer, these studies were carried out from PSG IAS, Coimbatore, Tamil Nadu, India.

## 3. RESULTS AND DISCUSSION

### 3.1. XRD Analysis:

The X-Ray Diffraction analysis technique was used to identify the crystalline nature and the structural properties i.e., size, and chemical composition of synthesized material[9].

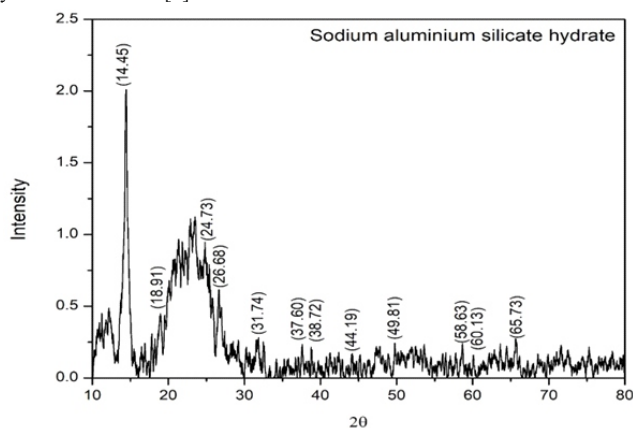


Figure 4. XRD pattern of Sodium Aluminium Silicate Hydrate Nanocrystals

Figure (4) shows the XRD pattern of sodium aluminium silicate hydrate nanocrystals which exhibits the position of diffraction peaks corresponding to the 2θ value of (14.45), (18.91), (24.73), (31.74), (37.60), (38.72), (44.19), (49.81), (58.63), (60.13) and (66.73) which was assigned to lattice planes of (110), (200), (211), (310), (222), (321), (330), (442), (440), (530) and (611) respectively which matches with the sodium aluminium silicate hydrate crystal structure (Chemical formula:  $\text{Na}_x(\text{AlSiO}_3)_y \cdot 8\text{H}_2\text{O}$ ) and was in well agreement with JCPDS No. 00-031-1271 which corresponds to sodium aluminium silicate hydrate nanocrystals, Crystal system: Cubic[4],[6] XRD pattern shows that all diffraction peaks were sharp which confirms that the prepared sample of sodium aluminium silicate hydrate has a crystalline phase[10]. The average crystallite size was determined using Debye Scherrer's formula,

$$D_{\text{nd}} = k \lambda / \beta \cos \theta$$

where,  $D_{\text{nd}}$  – average crystallite size,  $k$  – Debye constant (0.9),  $\lambda$  – wavelength of X-ray,  $\beta$  – full width half maximum of diffraction peak,  $\theta$  – the diffraction angle. It was found that the average crystallite size of prepared sodium aluminium

silicate hydrate was ~17 nm.

### 3.2. UV-Visible Analysis:

The UV-visible spectroscopy technique was used to analyse the size, agglomeration state, concentration and optical properties of prepared materials[9].

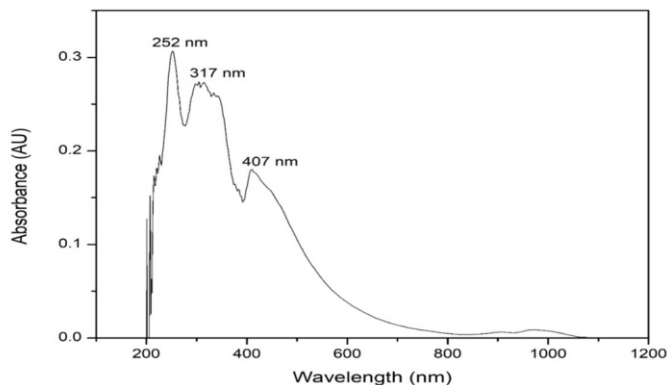


Figure 5. UV spectra of Sodium Aluminium Silicate Hydrate Nanocrystals

Figure 5 exhibits the UV optical absorption spectrum of sodium aluminium silicate hydrate nanocrystals. A strong absorption peak at 252 nm was followed by a weak peak at 317 nm and shoulder peak at 407 nm. These peaks showed the maximum absorbance in the UV region at below 450 nm, this confirms that the absorbance was in blue shift region[11]. The band gap values estimated to these maxima are from the UV cut-off of Sodium Aluminium Silicate Hydrate Nanocrystals is found to be 4.92 eV, 3.91 eV, 3.05 eV respectively.

### 3.3. EDAX Analysis:

The Energy Dispersive X-ray Analysis technique was used to check the presence of elemental and chemical composition in the prepared sample[9].

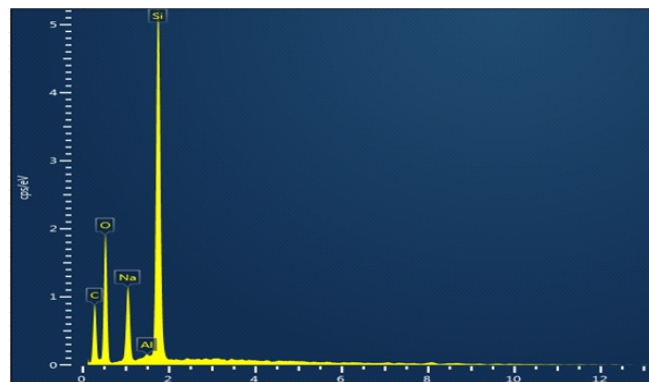


Figure 6. EDAX spectrum of Sodium Aluminium Silicate Hydrate Nanocrystals

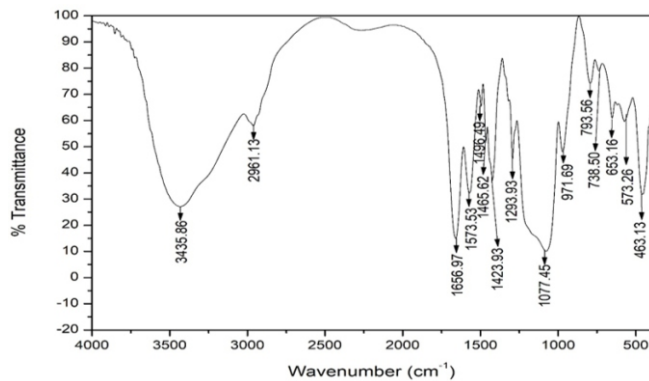
Figure (6) shows the EDAX result for the prepared Sodium Aluminium Silicate Hydrate Nanocrystals. EDAX data furnish that the prepared sample contains carbon, oxygen, silica, sodium and aluminium. Presence of negligible amount of Al may be due to aluminium foil which is used to cover the beaker and petri dish throughout the process, as aluminium foil contains 99.4% of aluminium[12]. Aluminium leaches into particles in acidic solution when heat is applied[13]. Presence of carbon may be due to the usage of carbon conducting tape present in the EDAX machine Jeol 6390LA/ OXFORD XMX N which was Ravi Kant Sharma and Ranjana Ghose also noticed the carbon in their work during the preparation of nanocrystalline CuO-ZnO mixed metal oxide powder prepared by homogeneous precipitation method[14].

Thus, from the above EDAX spectrum, the required composition was achieved without any impurity traces.

Element	Molecular wt. %	Atomic wt. %
C	33.54	46.23
O	30.85	31.92
Na	6.61	4.76
Al	0.11	0.07
Si	28.88	17.02

### 3.4. FTIR Analysis:

The Fourier Transform Infra-Red spectroscopy technique was used to analyse the surface composition and ligand binding in prepared sample[9].

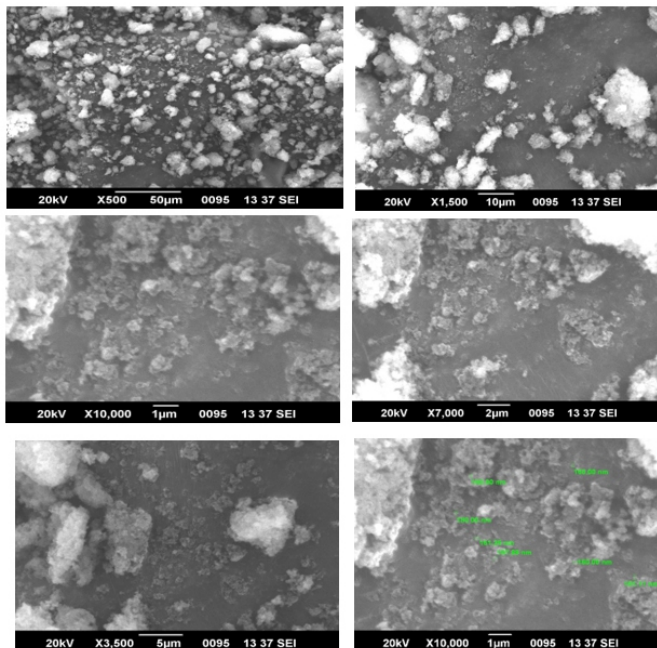


**Figure 7. FTIR spectra of Sodium Aluminium Silicate Hydrate Nanocrystals**

Figure (7) represents the FTIR spectra for the prepared sodium aluminium silicate hydrate nanocrystals. From the Figure (7) the band at  $463.13\text{ cm}^{-1}$  was assigned to Y-O-Y bending vibration (Y= Al and/or Si)[5]. The band noticed at  $573.26\text{ cm}^{-1}$  may be attributed to double ring vibration[5][6]. The band noticed at  $653.16\text{ cm}^{-1}$  corresponds to the internal Y-O-Y symmetric vibrations[5]. The bands which were located at  $738.50\text{ cm}^{-1}$  and  $793.56\text{ cm}^{-1}$  was attributed to the external Y-O-Y symmetric vibrations[5]. The band which was located at  $971.69\text{ cm}^{-1}$  was assigned to the internal Y-O-Y asymmetric vibration[5]. The band at  $1077.45\text{ cm}^{-1}$  corresponds to asymmetric stretching vibration of Y-O-Y and Si-O-Si bridging[15]. The bands at  $1423.88\text{ cm}^{-1}$ ,  $1465.62\text{ cm}^{-1}$  and  $1496.49\text{ cm}^{-1}$  corresponds to external Y-O asymmetric stretching vibration[6]. Furthermore the peaks at  $1656\text{ cm}^{-1}$  and  $3435\text{ cm}^{-1}$  corresponds to bending and stretching vibration of absorbed water molecules and C-H group in the sample respectively [15][6][4].

### 3.5. SEM Analysis:

The Scanning Electron Microscope analysis technique was used to identify the structural properties (size), agglomeration state and size distribution[9].

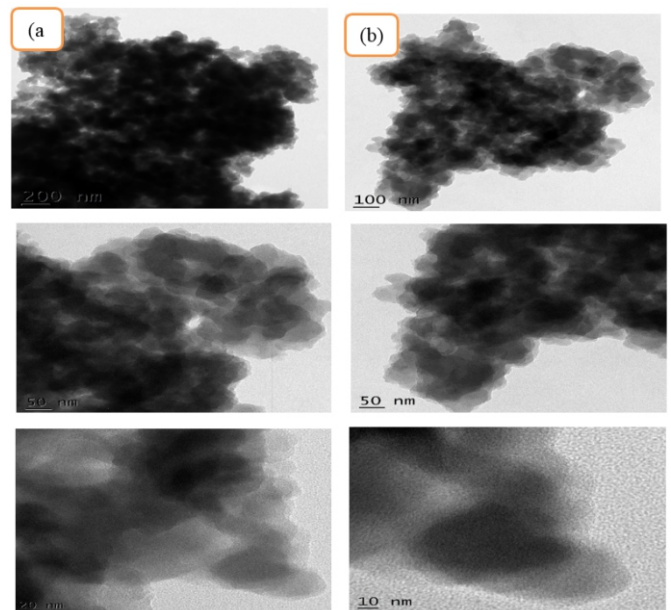


**Figure 8. SEM images of prepared Sodium Aluminium Silicate Hydrate Nanocrystals**

The SEM images of prepared sodium aluminium silicate hydrate Nanocrystals were found to be spherical in shape with irregular size, the overall surface was noticed to be spongy[5]. During the  $50\mu\text{m}$  of magnification it appears to be spongy, when the magnification increases to  $1\mu\text{m}$  it shows spherical shape. Due to the process of aging time and temperature treatment large particles are formed which may be due to agglomeration[16].

### 3.6. HR-TEM Analysis:

The High Resolution Transmission Electron Microscope analysis technique was used to identify crystal structure, single particle properties, structural properties (size) and structural defects[9].

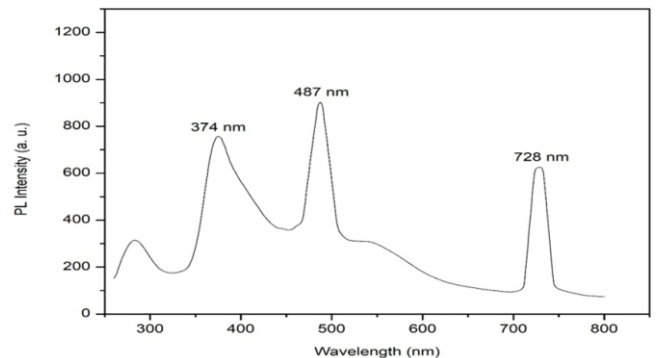


**Figure 9. HR-TEM images of Sodium Aluminium Silicate Hydrate Nanocrystals**

Figure (9) depicts the HR-TEM images of prepared sodium aluminium silicate hydrate Nanocrystals. The Figure (9a) and (9b) shows an agglomeration of cluster Nanocrystals. Other images shows the level of breakdown of agglomerated Nanocrystals according to different magnification and distribution of morphology with blurred spherical particle[17][5]. Overall, the Figure (9) clearly shows that the prepared sodium aluminium silicate hydrate nanocrystals was irregular spherical in shape. However, the HR-TEM images shows the composition of spherical with irregular shapes which was well correlated with the SEM image Figure (8). The agglomeration of nanocrystals were due to the presence of water molecules and ethanol in the prepared sample[1].

### 3.7. Photoluminescence Analysis:

The Photoluminescence Analysis technique was used to analyse the optical properties and relation to structure features i.e., defects, composition and size of prepared materials[9].



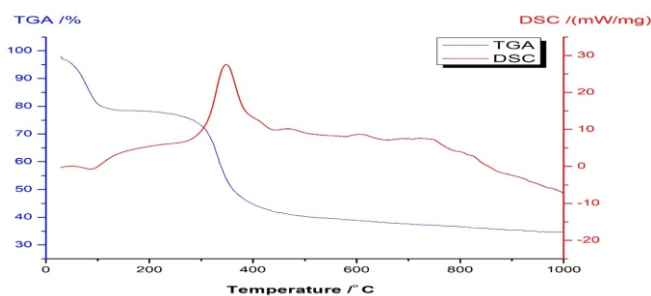
**Figure 10. PL spectra of Sodium Aluminium Silicate Hydrate Nanocrystals**

Figure (10) shows the PL emission spectrum of prepared sodium aluminium silicate hydrate nanocrystals at about  $250\text{ nm}$  photoexcitation at room temperature. The PL spectrum consists of three main emission bands: a strong UV emission peak at  $374\text{ nm}$  which corresponds to the near band edge emission due to excitonic recombination of  $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  Nanocrystals; a blue band at  $487\text{ nm}$  which may be assigned to the surface defects in the  $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  Nanocrystals[17]; and a red band was noticed at  $728\text{ nm}$ . The peaks in the photoluminescence spectra noticed at  $374\text{ nm}$ ,  $487\text{ nm}$  and  $728\text{ nm}$  takes the optical band gap values  $3.32\text{ eV}$ ,  $2.55\text{ eV}$  and  $1.70\text{ eV}$  respectively. Thus, the wavelength in PL spectra was shifted from higher to lower.

### 3.8. Thermal Analysis:

The thermal analysis TGA was used to analyse the mass and composition of stabilizers whereas DSC was used to analyse the difference in the amount of heat required to increase the temperature of samples[9].





**Figure 11. TG-DSC of Sodium Aluminium Silicate Hydrate Nanocrystals**

Figure (11) shows the TG-DSC plot of prepared sodium aluminium silicate hydrate nanocrystals. The TGA clearly shows two-stage decomposition and DSC shows the exothermic peak at 347 °C. In TGA the first stage of decomposition, occurred at a temperature range approximately at 100 °C, corresponds to the loss of moisture content[18]. The weight loss in this stage is about 21.79%. The second stage of decomposition, occurred at the temperature range of 120 °C- 400 °C, is attributed to the initial breakdown of reactants[19]. The weight loss in this stage is about 29.95%. There was a negligible amount of weight loss was noticed above 400 °C-1200 °C. The total weight loss was about 51.74%. In DSC the exothermic peak noticed at 347 °C may be corresponding to the elimination of organic and inorganic materials obtained from the decomposition of Sodium Aluminium Silicate Hydrate Nanocrystals[14][18]. Above 400 °C, no endothermic peaks or exothermic peaks was noticed.

## CONCLUSION

$\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  nanocrystals were successfully synthesized using the Co-precipitation method. The particle and structural morphology were analysed using XRD, SEM and HRTEM. The average crystallite size was found to be ~17 nm. The SEM and HR-TEM studies showed that nanocrystals were spherical in shape with irregular sizes. The EDAX spectrum confirms the composition of elements which was in accord with XRD analysis. UV-Vis absorption spectrum revealed the presence of peaks in blue shift range with corresponding band gap values which confirms that the prepared material is in nano range. PL emission bands for  $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  Nanocrystals exhibited three emission bands with optical band gap energy is shifted from higher to lower. The Thermal analysis result showed that the total weight loss of  $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 8\text{H}_2\text{O}$  nanocrystals was upto 51.74% and above 400 °C to 1200 °C there was negligible amount weight loss was noticed.

## REFERENCES

1. I. A. Rahman and V. Padavettan, "Synthesis of Silica Nanoparticles by Sol-Gel : Size-Dependent Properties , Surface Modification , and Applications in Silica-Polymer Nanocomposites—A Review," vol. 2012, 2012, doi: 10.1155/2012/132424.
2. A. A. Rywak and J. M. Burlitch, "Sol - Gel Synthesis of Nanocrystalline Magnesium Fluoride : Its Use in the Preparation of  $\text{MgF}_2$  Films and  $\text{MgF}_2$  -  $\text{SiO}_2$  Composites," no. 15, pp. 60–67, 1996.
3. R. Subramanian, P. Shankar, S. Kavithaa, S. S. Ramakrishnan, P. C. Angelo, and H. Venkataraman, "Synthesis of nanocrystalline yttria by sol-gel method," Mater. Lett., vol. 48, no. 6, pp. 342–346, 2001, doi: 10.1016/S0167-577X(00)00324-4.
4. L. Rassouli, R. Naderi, M. Mahdavian, and A. M. Arabi, "Synthesis and Characterization of Zeolites for Anti-corrosion Application : The Effect of Precursor and Hydrothermal Treatment," J. Mater. Eng. Perform., no. Ref 21, 2018, doi: 10.1007/s11665-018-3602-5.
5. M. A. Almutairi, F. K. Algethami, and H. M. Youssef, "Facile fabrication of novel analcime / sodium aluminum silicate hydrate and zeolite Y / faujasite mesoporous nanocomposites for efficient removal of  $\text{Cu}(\text{II})$  and  $\text{Pb}(\text{II})$  ions from aqueous media," Integr. Med. Res., vol. 9, no. 4, pp. 7900–7914, 2020, doi: 10.1016/j.imr.2020.05.052.
6. E. A. Abdelrahman, "Synthesis of zeolite nanostructures from waste aluminum cans for efficient removal of malachite green dye from aqueous media," J. Mol. Liq., vol. 253, pp. 72–82, 2018, doi: 10.1016/j.molliq.2018.01.038.
7. M. Chigondo et al., "Synthesis and Characterisation of Zeolites From Coal Fly Ash (CFA)," IRACST - Eng. Sci. Technol. An Int. J., vol. 3, no. 4, pp. 714–718, 2013.
8. D. Sridev and K. V. Rajendran, "Synthesis and optical characteristics of  $\text{ZnO}$  nanocrystals," Bull. Mater. Sci., vol. 32, no. 2, pp. 165–168, 2009, doi: 10.1007/s12034-009-0025-9.
9. S. Mourdikoudis and R. M. Pallares, "Characterization techniques for nanoparticles : comparison and complementarity upon studying," pp. 12871–12934, 2018, doi: 10.1039/c8nr02278j.
10. I. Journal, S. Engineering, and A. Science, "Synthesis of nanocrystalline  $\text{ZnCeO}_2$  by sol-Gel method," no. 3, pp. 9–11, 2016.
11. R. Mithra\* S. Venkateshwari\*\*, "GREEN SYNTHESIS OF ZINC CARBONATE HYDROXIDE NANO PARTICLES USING ELEOCARPUS TECTORIS," J. Phys. A Math. Theor., vol. 44, no. 8, pp. 9–25, 2011, doi: 10.1088/1751-8113/44/8/085201.
12. M. K. Teknologi, "Jurnal iptek," pp. 129–136, 2021, doi: 10.31284/j.iptek.2021.v25i2.
13. M. A. Hussein and K. W. S. Al-janabi, "Study of Main Factors Affecting the Leakage of Aluminum into the Food Wrapped in Aluminum Foil During Cooking," 2021, doi: 10.25258/ijddt.11.4.68.
14. R. K. Sharma and R. Ghose, "Synthesis of nanocrystalline  $\text{CuO}$  -  $\text{ZnO}$  mixed metal oxide powder by a homogeneous precipitation method," Ceram. Int., vol. 40, no. 7, pp. 10919–10926, 2014, doi: 10.1016/j.ceramint.2014.03.089.

15. T. M. A. Ellateif and S. Maitra, "Some studies on the surface modification of sol-gel derived hydrophilic Silica nanoparticles," vol. 8, no. 2, pp. 97–106, 2017, doi: 10.22034/ijnd.2017.25013.
16. R. Stanley and a S. Nesaraj, "Effect of Surfactants on the Wet Chemical Synthesis of Silica Nanoparticles," no. October 2013, pp. 9–21, 2014.
17. A. A. Baqer, K. A. Matori, N. M. Al-Hada, A. H. Shaari, E. Saion, and J. L. Y. Chyi, "Effect of polyvinylpyrrolidone on cerium oxide nanoparticle characteristics prepared by a facile heat treatment technique," Results Phys., vol. 7, pp. 611–619, 2017, doi: 10.1016/j.rinp.2017.01.020.
18. C. Wang et al., "Int . Journal of Refractory Metals and Hard Materials Synthesis of monodispersed  $\text{La}_2\text{Ce}_2\text{O}_7$  nanocrystals via hydrothermal method : A study of crystal growth and sintering behavior," RMHM, vol. 31, no. 3, pp. 242–246, 2012, doi: 10.1016/j.jrmhm.2011.12.002.
19. L. K. Babu and Y. V. R. Reddy, "A Novel Thermal Decomposition Approach for the Synthesis and Properties of Superparamagnetic Nanocrystalline  $\text{NiFe}_2\text{O}_4$  and Its Antibacterial, Electrocatalytic Properties," J. Supercond. Nov. Magn., vol. 33, no. 4, pp. 1013–1021, 2020, doi: 10.1007/s10948-019-05262-x.